



US006538056B1

(12) **United States Patent**
Webster(10) Patent No.: **US 6,538,056 B1**
(45) Date of Patent: **Mar. 25, 2003**(54) **POLYOLEFIN ARTICLES WITH LONG-TERM ELEVATED TEMPERATURE STABILITY**(75) Inventor: **Joseph R. Webster, Charlotte, NC (US)**(73) Assignee: **Clariant International Ltd., Muttentz (CH)**

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/685,314**(22) Filed: **Oct. 10, 2000**(51) Int. Cl.⁷ **C08K 3/30; C08K 5/34; C08K 5/15; C08K 5/53; C08K 5/09**(52) U.S. Cl. **524/418; 524/96; 524/100; 524/101; 524/108; 524/131; 524/146; 524/153; 524/199; 524/232; 524/248; 524/291; 524/336; 524/343; 524/349; 524/359**(58) Field of Search **524/418, 96, 100, 524/101, 131, 108, 146, 153, 199, 232, 248, 291, 330, 343, 349, 359**(56) **References Cited****U.S. PATENT DOCUMENTS**

3,344,113 A	9/1967	Alheim et al.	
3,511,802 A	5/1970	Newland et al.	
3,644,482 A	2/1972	Dexter et al.	
3,681,417 A	8/1972	Simons	
3,684,765 A	8/1972	Matsui et al.	
3,894,838 A	7/1975	von der Eltz et al.	
3,944,594 A	3/1976	Kleiner et al.	
4,012,192 A	3/1977	Doerr	
4,239,803 A	* 12/1980	Ohzeki et al.	428/379
4,251,282 A	2/1981	Vahlensieck et al.	
4,251,650 A	2/1981	Mietzsch et al.	
4,343,653 A	8/1982	Beach et al.	
4,366,271 A	12/1982	Riegler	
4,367,307 A	1/1983	Hirai et al.	
4,925,889 A	5/1990	Capolupo et al.	
4,976,889 A	12/1990	Aumuller et al.	
4,985,480 A	1/1991	Fukui et al.	
4,992,078 A	2/1991	Meszaros	
5,086,173 A	2/1992	Tritschler	
5,098,945 A	3/1992	Pitteloud et al.	
5,199,957 A	4/1993	Pascoe	
5,214,084 A	* 5/1993	Ishii et al.	524/96
5,240,466 A	8/1993	Bauer et al.	
5,300,148 A	4/1994	Domingo et al.	
5,326,622 A	7/1994	Yamane et al.	
5,376,290 A	12/1994	Meier et al.	
5,383,961 A	1/1995	Bauer et al.	
5,470,356 A	11/1995	Meszaros	
5,571,899 A	11/1996	Kaul et al.	
5,618,909 A	4/1997	Lofquist	
5,705,545 A	1/1998	Avar et al.	
5,851,238 A	12/1998	Gadoury et al.	
5,874,493 A	2/1999	Webster	
5,932,640 A	8/1999	Kaul et al.	
5,965,261 A	10/1999	Webster	
5,969,014 A	10/1999	Webster et al.	

6,019,800 A	* 2/2000	Hipp et al.	8/640
6,063,843 A	5/2000	Sidqi et al.	
6,126,736 A	10/2000	Stoll et al.	
6,153,676 A	11/2000	Avar et al.	
6,197,274 B1	3/2001	Mahmud et al.	
6,201,047 B1	3/2001	Avar et al.	
6,218,452 B1	4/2001	Kaul et al.	
6,262,153 B1	7/2001	Webster et al.	

FOREIGN PATENT DOCUMENTS

CA	843985	6/1970
DE	3233953 A1	3/1984
DE	4012449 A1	10/1991
EP	0325172 B1	7/1989
EP	0417017 B1	3/1991
EP	0675160 A2	10/1995
GB	419445	4/1933
GB	820207	10/1959
GB	2292559	2/1996
JP	3-207733	9/1991
WO	95/28443	10/1995
WO	97/05189	2/1997
WO	97/43335	11/1997

OTHER PUBLICATIONS

U.S. patent application Ser. No. 08/518,625, filed Aug. 23, 1995, Sanahuja.

U.S. patent application Ser. No. 09/141,893, filed Aug. 28, 1998, Webster et al.

English Abstract of DE 4012449; Oct. 24, 1991.

English Abstract of DE 3233953; Mar. 15, 1984.

English Abstract of JP 03-207733; Sep. 11, 1991.

English Abstract of JP 6010276 A; Jan. 18, 1994.

English Abstract of JP 60-042441; Mar. 06, 1985.

Harkins et al., "Synergistic Antioxidant Combinations. Mechanism of Stabilization with Organo-Sulfur Compounds" pp. 3499-3509, "Journal of Polymer Science: Part A", vol. 1; 1963.

Stengrevics et al., "Stabilization of Filled Polyolefins"; pp. 35-39, from "Plastics Compounding", Jul. 1987.

(List continued on next page.)

Primary Examiner—Kriellion A Sanders(74) *Attorney, Agent, or Firm*—Anthony A. Bisulca(57) **ABSTRACT**

What is disclosed are polyolefin compounds, e.g., polyethylene and polypropylene, and articles therefrom made in by conventional solid, melt-phase compounding with oxidized, non-cationized, non-silylated sulfur black pigment, a phenolic antioxidant and a sulfur-containing secondary stabilizer, each in stabilizing amount, specified below, which provide a synergistic improvement in the long term heat aging of polyolefins. Preferably the sulfur black compound is treated by washing, and reduction in the soluble sodium salts.

Also disclosed is melt-phase compounded polyolefin and molded articles made therefrom comprising incorporating of carbon black, oxidized, non-cationized, non-silylated sulfur black pigment, a phenolic antioxidant and sulfur-containing secondary stabilizer.

21 Claims, 6 Drawing Sheets

Best Available Copy

2,2'-oxalyldiamidobisethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (NAUGARD XL 1);
 2,2'-methylenebis(4-ethyl-6-tert-butylphenol) (CYANOX 425);
 2,2'-methylenebis[6-(1-methylcyclocyclohexyl)-p-cresol];
 4,4'-thiobis(6-t-butyl-o-cresol);
 2,2'-thiobis[4,6-di-tert-butyl-m-cresol] (TOPANOL® TP);
 2,2'-thiobis[4,6-di-tert-butyl-o-cresol] (SANTANOX® R);
 4,4'-thiobis(3-methyl-6-t-butyl phenol) (IRGANOX 415) (SEENOX® BCS);
 thiobisdiethylenebis(3,5-di-t-butyl-4-hydroxy) hydrocinnamate (IRGANOX 1035);
 butyric acid, 3,3-bis(3-t-butyl-4-hydroxyphenyl) ethylene ester;
 2,2'-ethylidenebis(4,6-di-t-butylphenol);
 2,2'-thiobis(4-methyl-6-tert-butylphenol) (IRGANOX 1081);
 bis[4-(2-phenyl-2-propyl)phenyl] amine (NAUGARD 445);
 N,N-dimethyl(3,5-di-tert-butyl-4-hydroxybenzyl) amine (ETHANOX 703);
 4,4'-di-tert-octyldiphenylamine (VANOX 1081);
 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (NONOX® WSO); and
 1,6-hexamethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (IRGANOX L09);
 the polyphenols, like 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione;
 tetrakis[methylene(3,5-di-t-butyl-4-hydroxy) hydrocinnamate]methane;
 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazine-2,4,6-(1H, 3H, 5H)-trione (GOOD-RITE 3114);
 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate (CYANOX® 1790);
 trimethyl-2,4,6-tris(3,5, -di-t-butyl-4-hydroxybenzyl) benzene);
 tris(3,5, -di-t-butyl-4-hydroxybenzyl)isocyanurate;
 tris(3,5-di-tert-butyl-4-hydroxyphenyl)phosphate (ETHANOX ® 796);
 hydrocinnamic acid, 3,5-di-t-butyl-4-hydroxy-, triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6-(1H, 3H, 5H)-trione (GOOD-RITE® 3125);
 1,1,3-tris((2-methyl-4-hydroxy-5-t-butylphenyl)butane) (TOPANOL CA);
 3,5-bis((3,5-di-tert-butyl-4-hydroxy)benzyl)-2,4,6-trimethylphenol (IRGANOX® 1299);
 and pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (IRGANOX 1010);
 and other suitable antioxidants, including calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate) (IRGANOX 1425);
 o,o-dimethyl o-(4-cyanophenyl) phosphorothioate (SUMITOMO S 4084);
 terephthalic acid, 1,4-dithio-,S,S-bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)ester (CYANOX 1729);

triethylene glycol bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate)(AO 70);
 hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate (IRGANOX 259);
 1,2-bis(3,5, -di-tert-butyl-4-hydroxyhydrocinnamoyl) hydrazide (IRGANOX 1024);
 4,4'-di-tert-octyldiphenamine (NAUGALUBE® 438R);
 phosphonic acid, (3,5-di-tert-butyl-4-hydroxybenzyl)-, dioctadecyl ester (IRGANOX 1093);
 1,3,5-trimethyl-2,4,6-tris(3',5'-di-tert-butyl-4-hydroxybenzyl)benzene (IRGANOX 1330); 2,4-bis(octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine (IRGANOX 565); isooctyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (IRGANOX 1135);
 octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (IRGANOX 1076);
 3,7-bis(1,1,3,3-tetramethylbutyl)-10H-phenothiazine (IRGANOX LO 3);
 2,2'-methylenebis(4-methyl-6-tert-butylphenol) monoacrylate (IRGANOX 3052);
 2-tert-butyl-6-[1-(3-tert-butyl-2-hydroxy-5-methylphenyl)ethyl]4-methylphenyl acrylate (SUMILIZER TM 4039);
 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]4,6-di-tert-pentylphenyl acrylate (SUMILIZER GS);
 1,3-dihydro-2H-Benzimidazole (SUMILIZER® MB);
 2-methyl-4,6-bis[(octylthio)methyl]phenol (IRGANOX 1520);
 N,N'-trimethylenebis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide (IRGANOX 1019);
 4-n-octadecyloxy-2,6-diphenylphenol (IRGANOX 1063);
 2,2'-ethylidenebis[4,6-di-tert-butylphenol] (IRGANOX 129);
 N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide) (IRGANOX 1098);
 diethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate (IRGANOX 1222);
 4-octyl-N-(4-octylphenyl)-benzenamine (ANOX NS);
 4,4'-di-tert-octyldiphenylamine (IRGANOX 5057);
 N-phenyl-1-naphthalenamine (IRGANOX L 05);
 2,2,4-trimethyl-1,2-dihydroquinoline polymer (ANOX® HB);
 tris[2-tert-butyl-4-(3-ter-butyl-4-hydroxy-6-methylphenylthio)-5-methyl phenyl] phosphite (HOSTANOX OSP 1);
 zinc dinonyldithiocarbamate (HOSTANOX VP-ZNCS 1);
 and
 3,9-bis[1,1-diimethyl-2-[(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (SUMILIZER® AG80).
 The preferred antioxidants are pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, sold as HOSTANOX® O 10; 1,3,4-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4-(1H, 3H, 5H)-trione, or a mixture, and most preferred is 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4-(1H, 3H, 5H)-trione.
 The sulfur containing secondary antioxidant (C) are referred to as β -thioesters ($-S-C-C-C(O)-OR$) and